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Instrumental Achievements

Crystal Structure of 6-Amino-3-ethyl-1,2,4-triazolo[3,4-*f*][1,2,4]triazin-8(7*H*)-one

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The correct dominant tautomeric structure makes it possible to interpret the detailed mechanisms of reactions of tautomeric heterocycles properly. The correct dominant tautomeric structure also makes it possible to interpret the biological activity and functions of potential tautomeric heterocycles.[1] Many of these aza/deaza analogues of purine and their nuclosides have drawn considerable interest in biological activity. Compound 6-amino-1,2,4-triazolo[3,4-*f*][1,2,4]triazin-8-one (4,8-diaza-9-deazaguanine, **1**), the isosteric isomer of guanine, may retain the Watson–Crick type hydrogen bonding sites of the aglycon moiety. As a part of our ongoing program we studied the most contributing prototropic tautomerism of this bicycloheterocyclic moiety of compound **1**. We considered three tautomers: the amino-oxo forms 5*H*-tautomer (**1a**), 7*H*-tautomer (**1b**), and the amino-hydroxy form (**1c**), plus a rotamer (**1d**) (not considering improbable imino forms) (Fig. 1). To our knowledge, this issue has never been discussed in the literature. A clear-cut answer is the use of X-ray crystallography analysis, which provides precise information about the most stable structure among tautomers. In the present paper, we report on the crystal structure of the title compound based on a single-crystal X-ray analysis.

A chunky colorless crystal suitable for single-crystal X-ray diffraction measurements of the title compound 6-amino-3-ethyl-1,2,4-triazolo[3,4-*f*][1,2,4]triazin-8(7*H*)-one (**2**) (Fig. 1) was obtained by recrystallization from H_2O solution. The compound **2** prepared by the method of Lovelette[2] was one of the 3-substituted derivative compounds of **1** that we had synthesized. The results of the X-ray structure determination are given in Tables 1 and 2. The ORTEP drawing for the title compound is shown in Fig. 2.

From this X-ray analysis of the title compound, the structural framework is constructed from the 1,2,4-triazole five-membered ring fused at C(1)–N(5) with a distorted 1,2,4-triazinone six-membered ring, which bears an H_2O molecule by a intermolecular hydrogen bond. Meanwhile, it has been clarified

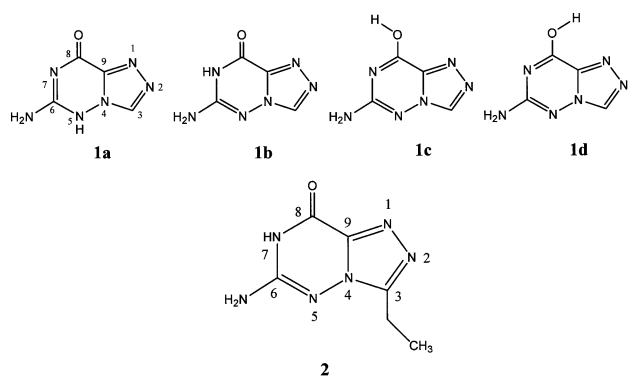

Fig. 1 The amino form tautomers (**1a** – **1d**) of 6-amino-1,2,4-triazolo[3,4-*f*][1,2,4]triazin-8-one, and the chemical structure of the title compound (**2**) with atom-numbering scheme.

Table 1 Crystal and experimental data for 6-amino-3-ethyl-1,2,4-triazolo[3,4-*f*][1,2,4]triazin-8(7*H*)-one (**2**)

Formula: $C_6H_{10}N_6O_2$
Formula weight = 198.20
Crystal system: orthorhombic
Space group: $Pna2_1$ $Z = 4$
a = 8.7016(2)Å
b = 19.0851(4)Å
c = 5.48770(10)Å
V = 911.82(3)Å^3
D_{calc} = 1.444 g/cm^3
μ(Mo K$_\alpha$) = 0.113 mm^{-1}
T = 295(2)K
F(0 0 0) = 416
Crystal dimensions: 0.4 × 0.25 × 0.15 mm
θ range: 2.13 to 29.56°
h k l: –12/12, –25/25, –7/7
λ(Mo K$_\alpha$) = 0.71073 Å
No. of reflections measured = 11969
No. of independent reflections = 2421 (R_{int} = 0.0303)
No. of observed reflections = 2068 [$I > 2\sigma(I)$]
Absorption correction: SADABS[3]
Data/restraints/parameters: 2421/1/168
Goodness-of-fit on F^2 = 1.107
Final R indices: $R1$ = 0.0428, $wR2$ = 0.1028
R indices (all data): $R1$ = 0.0537, $wR2$ = 0.1088
$(\Delta/\sigma)_{max}$ = 0.003
$(\Delta\rho)_{max}$ = 0.161 eÅ^{-3}
$(\Delta\rho)_{min}$ = –0.151 eÅ^{-3}
Measurement: Siemens SMART CCD
Program system: SAINT
Structure determination: direct methods (SHELXS-86)[4]
Refinement: full-matrix least-squares (SHELXL-93)[5]

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq}
N(1)	10613 (2)	7037 (1)	5428 (3)	43 (1)
N(2)	9992 (2)	7642 (1)	4437 (3)	43 (1)
N(3)	7473 (2)	7422 (1)	– 764 (3)	37 (1)
N(4)	8379 (2)	6319 (1)	707 (3)	40 (1)
N(5)	9156 (2)	6728 (1)	2395 (3)	36 (1)
N(6)	6764 (2)	6373 (1)	– 2561 (4)	53 (1)
C(1)	9121 (2)	7436 (1)	2621 (3)	36 (1)
C(2)	8216 (2)	7843 (1)	900 (4)	37 (1)
C(3)	7560 (2)	6695 (1)	– 792 (3)	37 (1)
C(4)	10102 (2)	6490 (1)	4173 (4)	41 (1)
C(5)	10500 (3)	5739 (1)	4497 (5)	52 (1)
C(6)	11789 (3)	5628 (1)	6307 (5)	56 (1)
O(1)	8102 (2)	8477 (1)	885 (3)	53 (1)
O(2)	9298 (3)	9889 (1)	1512 (4)	74 (1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

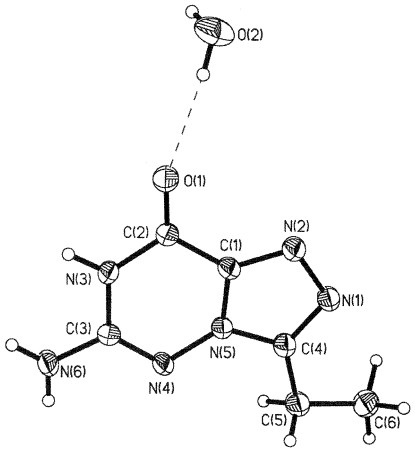

Fig. 2 ORTEP drawing of 6-amino-3-ethyl-1,2,4-triazolo[3,4-*f*]-[1,2,4]triazin-8(7*H*)-one (**2**).

that the predominant tautomeric structure is amino-oxo form 7*H*-tautomer. The intermolecular hydrogen bond lies between O(1) and O(2)–H(2A) [O(1)··O(2) = 2.909 Å, O(1)··H(2A) = 2.086 Å, O(2)–H(2A) = 0.823 Å, O(2)–H(2B) = 0.904 Å, O(2)–H(2A)··O(1) = 174.7°]. In H_2O molecule the 0.081 Å deviation of bond length between O(2)–H(2A) and O(2)–H(2B) is due to the hydrogen bonding attraction. The structure of the bicycloheterocyclic [1,2,4]triazolo[3,4-*f*][1,2,4]triazinone ring reveals obvious distortion, and the short bonds 1.304(2)Å (C(3)–N(4)), 1.312(2)Å (C(1)–N(2)) and 1.327(2)Å (C(4)–N(1)) in the ring have an appreciable double-bond character. The 3-ethyl substituted group shows an exoextensibility. The 6-amino substituted group's bond length 1.341(2)Å between C(3)–N(6) is shorter than those of 1.359(2)Å (C(1)–N(5)), 1.378(2)Å (C(2)–N(3)), 1.390(2)Å (C(3)–N(3)) and 1.355(2)Å (C(4)–N(5)) in the bicycloheterocyclic ring. Evidently, the 6-amino group strongly donates the unpaired electrons and resonates with the [1,2,4]triazolo[3,4-*f*][1,2,4]triazinone ring.

Acknowledgements

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